Energy Storage Performance of Hydrogen Fuel Cells Operating in a Marine Salt Spray Environment using Experimental Evaluation

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Abstract: In a marine salt spray environment, sodium chloride poisoning will significantly deteriorate the performance of the hydrogen fuel cells; for example, proton exchange membrane fuel cells (PEMFCs). Currently, the degradation mechanisms of the PEMFC caused by the sodium chloride poisoning are often evaluated by the pollution of the F ions;

however, the pollution of the sodium chloride in the membrane electrodes is seldomly inspected. In this avail, this work experimentally explores the influence of the sodium chloride pollution on the PEMFC performance in the marine salt spray environment by analyzing the concentration diffusion characteristics of the sodium chloride in the PEMFC membrane electrodes. Firstly, a set of experiments were carried out to determine the distribution of the sodium chloride components in the membrane electrodes, where five different salt spray environments (i.e., 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, and 500 mg/L of the salt component, respectively) were used/employed to analyze the concentration diffusion characteristics of the sodium chloride. Then, the obtained samples were microscopically characterized and elementally analyzed by the field emission scanning electron microscopy (FESEM) and the energy spectrometry. Subsequently, a least squares-based model was proposed to predict the diffusion rate of the contaminating ions in the membrane electrodes. Lastly, the pollution of the sodium chloride was evaluated/assessed to reveal the performance degradation of the PEMFCs. The experimental results demonstrated that (1) the sodium chloride fraction existed as crystals or ions in the membrane electrodes in the marine salt spray environment; (2) the sodium chloride poisoning was founded in the proton exchange membrane in the form of sodium ions; (3) and the sodium-to-chloride ratio was proportional to the contamination time and the salt spray in the proton exchange membrane.

Keywords: Hydrogen fuel cells; proton exchange membrane fuel cell; membrane electrode; salt spray test

1. Introduction

The proton exchange membrane fuel cell (PEMFCs) ~~is a typic type of hydrogen fuel cells and~~ has been an emergent alternative to fossil fuels in the marine power systems because of high practicability and low emissions and environmental pollution. However, in a marine salt-spray environment, the sodium and chloride concentrations are much higher than these in the inland areas, which results in that the sodium chloride poisoning frequently occurs in the PEMFCs to cause an irreversible decay on the PEMFCs performance [1, 2]. The term "sodium chloride poisoning" was introduced by Mikkola [3], who found that the sodium chloride can damage the catalyst in the PEMFCs and lead to degradation of battery performance. Unnikrishnan et al. [4] stated that the

chlorine contamination can cause performance loss on the battery anode and cathode by 94 % and 82 %, respectively. Therefore, it is critical to study the mechanism of sodium chloride poisoning in marine salt spray environment to prevent battery degradation.

The durability of the proton exchange membrane is one of the most important indicators of cell performance, and proton exchange membrane operation is subject to contamination from various materials in the cell stack, coolant, and fuel-side contaminants [5]. Impurities from the air side enter the cathode side of the PEMFC, where they dissolve in liquid water and penetrate the cathode side under a concentration gradient, causing degradation or failure of the cell during operation [6]. And for the sodium chlorine poisoning, when the chlorine enters the PEMFC the chlorine ions are adsorbed on the catalyst Pt surface, which may damage the catalyst. Literature review indicates that impurities have been found to degrade cell performance by affecting the H^+ content and the active specific surface area of the catalytic layer [7] and the degree of contamination is usually evaluated in terms of the release rate of F ions, the atomic percentage and the migration rate of impurities. Recent progress suggests that the membrane cation contamination is an important cause of the battery degradation. For example, Wang et al. [7] investigated the degree of contamination of the membrane electrode components by immersion experiments in perionic solutions (Ca^{2+}, Mg^{2+}, Na^+), studied the effect of the contaminated solution environment on the catalytic and gas diffusion layers, and found that the H^+ in the proton exchange membrane was more contaminated by metal cations than the catalytic layer. Jie et al. [8] found that the presence of Na+ had a significant toxic effect on the Pt/C In 2009, Strmcnik et al [9] proposed a cluster of non-covalent interactions between Pt and surface oxides on cations (containing Na+), leading to the occupation of Pt active sites in electrochemical reactions. Jayasayee et al [10] carried out a study on the relationship between Cl- concentration and dissolution rate of PtNi alloy by energy dispersive X-ray spectroscopy(EDX) and inductively coupled plasma spectroscopy and determined that Cl- enhanced the dissolution of Pt and Ni by monitoring the changes in the percentage of Pt and Ni atoms. Uddin et al. [11] analyzed the surface and cross-section of the gas diffusion layer of the cell membrane electrode and the cross-sectional morphology of the catalytic coating membrane (CCM) by Scanning electron microscopy **(**SEM) and energy dispersive X-ray spectroscopy **(**EDS), and the results showed that cations were not detected in the CCM, but the study indicated that chloride ions reduced the catalyst activity specific surface area.

Arruda T et al.[12]studied the competition of anion adsorption on the catalyst Pt surface by the spectra formed by XRD, EDX in a half-cell system. Mo et al. [13] analyzed the migration of corrosion product metal cations in PEMEC catalyst coating membranes with EDS images, showing that high levels of Fe cations in Nafion membranes occupied the water nanochannels in the membranes, reducing the proton transport efficiency in PEM. Gutleben et al. [14] showed that the degradation of Pt was caused by the electrochemical reaction of chloride in the vicinity of the membrane. The chemical degradation of the membrane is mainly due to the vulnerability of the SO_3H, CF_3, OCF_2 and CF groups on the side chains of the perfluoro sulfonic acid polymer to attack by (-OH) radicals and shedding, resulting in the destruction of the function and integrity of the proton exchange membrane [15, 16]. Hori et al. [17] studied the dissociation of F- from fluorine elements in membranes after immersion in a contaminated solution containing iron, along with the appearance of intermediate products in the membrane side chains. Zhang et al. [18] showed that the rate of fluorine ion release from membranes was linearly and positively correlated with the time of contamination. Kelly et al. [19] evaluated the degree of membrane contamination by determining the calculated ion uptake in membranes based on the concentration of cationic impurities and by energy dispersive X-ray analysis through the atomic percentage ratio. Inaba et al. [20] studied the rate of reaction between air and hydrogen at the fuel side to generate free radicals, the rate of release of fluorine ions by to compare the fast rate of generation of fluorine ions on the anode side and the cathode side. Liu et al [21] found by in situ detection method that the anode produced free radicals diffused to the cathode side through the concentration difference thus leading to the attenuation of the proton film. By in situ detection method, it was found that the anode produced free radicals diffused to the cathode side through the concentration difference thus leading to the decay of the proton film. Kienitz et al. [22] investigated the degradation of the performance of a proton exchange membrane fuel cell contaminated with foreign cations (Na^+, Ca^{2+} or metal ions) in a half-cell model by numerical simulations, and evaluated the contaminant and proton transport through diffusion and migration by comparing the rate of release of fluoride ions from the anode side and the cathode side. Xie et al. [23] evaluated the degree of contamination by observing the crack expansion of the membrane through electron micrographs and performed molecular simulations of weight loss and product emission rates as time to model the chemical contamination degradation and mechanical deformation of the membrane. Md Aman Uddin

et al. [24] investigated the effect of the gas diffusion layer (GDL) on cationic contamination of polymer electrolyte fuel cells (PEFCs) by soaking three membrane electrode assembly (MEA) structures in cationic (Ca^{2+}) solution. The results showed that the hydrophobicity of GDL and microporous layer (MPL) was a barrier to the cationic solution reaching CCM.

In summary, ~~although existing literatures have indicated that the contamination of the membrane electrode components causes absolute PEMFC degradation, very limited work has been done to address the PEMFC degradation mechanisms in the marine salt-spray environment.~~ for the PEMFC-powered ships, it is inevitable to investigate on the influence of the sodium chloride on the membrane electrodes and explore the PEMFC degradation mechanisms. However, there is little work on this in existing literatures.~~little work has been done yet.~~ To this end, this study examines the effects of the diffusion rate and contamination of the sodium chloride in the membrane electrodes to explore the battery degradation in the marine salt-spray environment. The evaluation of the contamination degree provides a theoretical basis for addressing the adverse effects of impurity ions on the battery and implications for the development of battery contamination mitigation strategies in the marine salt-spray environment.

The remainder of this paper is organized as follows. Experimental test of the sodium chloride pollution on the PEMFC membrane electrodes in the marine salt-spray environment is carried out in Section 2. In Section 3, the experimental results are presented. The evaluation of the contamination level of Na^+ in the membranes is performed in Section 4. Conclusions and future works are summarized in Section 5.

2. Experimental Materials and Results

2.1 Experiment Preparation

According to the operation of salt spray aerosol and the principle of salt spray generation, based on the conditions of the marine atmospheric environment parameters, the marine environment is simulated through the standard salt spray test chamber, where the salt spray particle size is between 0.1μm and 0.5μm, the salt spray concentration is between 100mg/m^3 and 500mg/m^3, the temperature is between 25℃ and 45℃, the humidity is between 85%RH and 95%RH, and the settling volume is between 1ml/80cm^2/h and 2ml/80cm^2/h. Accelerating test and natural atmospheric exposure test are carried out by loading the salt spray contents with different ratios, and refer to [25], the salt mist

content ranges between 0.2mg/m^3 and 0.66mg/m^3. Fig. 1 manifests the experimental test procedure, where the gas phase test is carried out to evaluate the sodium and chloride contamination effect on the battery membrane electrodes. The experimental procedure is described as follows.[26-27].

(1) Prepare the experimental membrane electrodes. Firstly, a 5cm × 5cm membrane electrode is divided into five 1cm × 5cm membrane electrode samples. The mass of each sample is weighed with an analytical balance. Then each sample is put into a vacuum drying oven at 80°C for 8 hours and baked until its mass is constant.

(2) Prepare the salt spray test solution. Firstly, dissolve the pure sodium chloride into the tertiary water in accordance with GBl266(GBl266: specifies the configuration of chemical reagent neutral salt spray solution) and GB6682(GB66829: specifies the water specifications and experimental methods for the analysis laboratory); and then, test the PH value of the obtained solution at 25℃ and ensure its PH value is between 6.5 to 7.5 to generate the neutral solution. After that, the neutral solution is deionized with impedance of 18Ω and mixed with the NaCl powder (purity of 99 %) to prepare five different concentrations of salt spray test solutions (i.e., 100mg/L, 200mg/L, 300mg/L, 400mg/L, and 500mg/L of the NaCl).

(3) Perform the gas phase test. Firstly, the 100mg/L NaCl solution is atomized and tested for 15 days. Then repeat the test using different concentrations to generate 30 membrane electrode samples in total for characteristics analyses. Lastly, the liquid nitrogen embrittlement is used to cut the electrode samples into 1cm × 1cm flat section to feed the SEM and EDS equipment. A Quorum sputter coater is used to pre-treat the samples to ensure accurate elemental analysis. A field emission electron microscope and an energy dispersive X-ray spectrometer Smart EDX are used to analyze the CCM of the catalyst coated membranes and the surface microscopy of the gas diffusion layer (GDL).

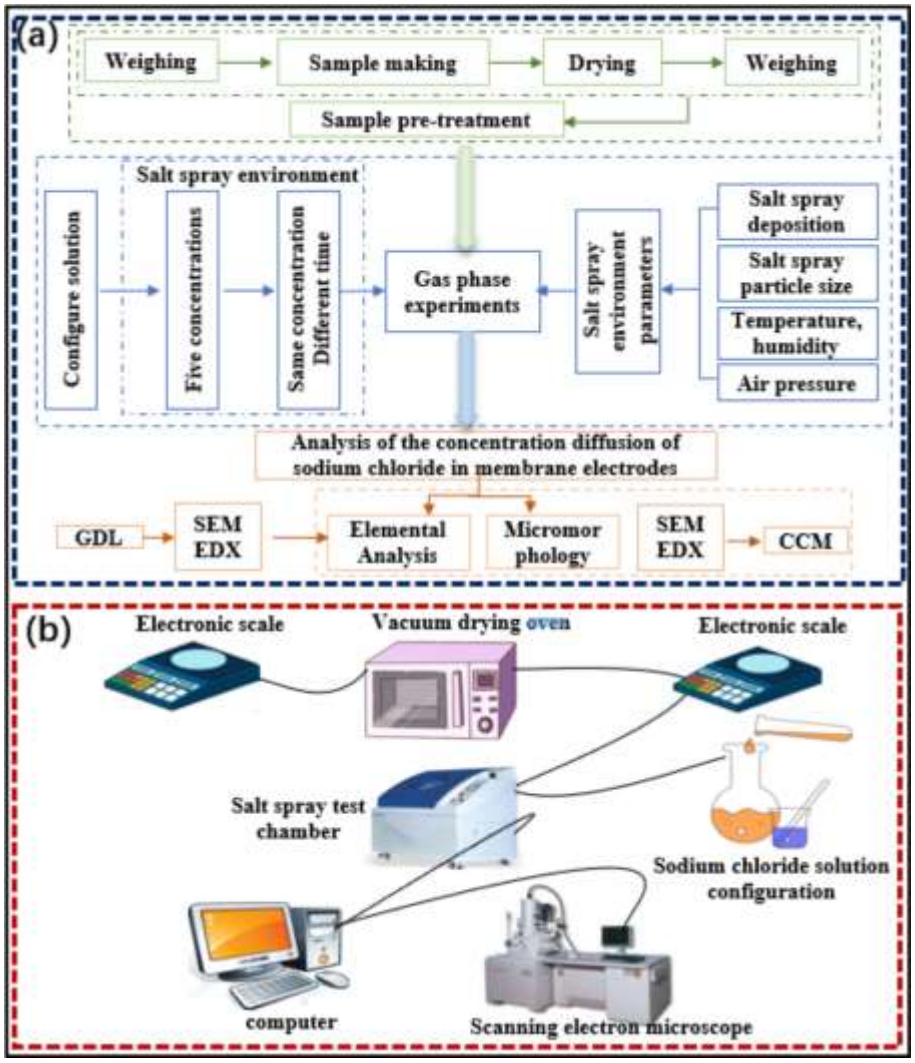


Fig. 1. Overview of experimental test.

In Fig. 1, the membrane electrodes (platinum loading volume: cathode 0.3mg/cm^2 & anode 0.1mg/cm^2) are produced by Wuhan Polytechnic New Energy Co. Ltd; the sodium chloride (99% purity) is produced by Tianjin Zhiyuan Chemical Reagent Co. Ltd; the vacuum drying oven (model DZF-6020) and electronic analytical balance (model FA2204) are provided by Shanghai Lichenbangxi Instrument Technology Co. Ltd; the KD-60 standard salt spray chamber is provided by Zhejiang Blue Arrow Instrument Co. Ltd; the German Zeiss field emission electron microscope (model SUPRA 55) and the energy dispersive X-ray spectrometer Smart EDX are used; the Quorum SC7620 sputter coater is supplied by Nanjing Qinshi Technology Co. Ltd.

2.2 Microscopic Morphological Characterization

The presence of sodium chloride and its distribution in the membrane electrode are analyzed by a combination of micromorphology and elemental analyses. In order to examine the effect of the

experiment time on the surface morphology of the GDL and the microscopic effects of the sodium chloride diffusion, the membrane electrodes are tested with different periods. In the experimental tests the crystal formation is made independent of the solution saturation precipitation by setting that the solution concentration is much lower than the solution saturation points of crystallization and precipitation. In addition, the experimental impurities are derived from the independent variable sodium chloride, and the deionized water used for solution preparation has excluded other impurity components. Therefore, in the experiments the appearance of crystal particles is only from the sodium chloride in the salt spray environment.

The tested results the membrane electrodes with impurities are compared with that without impurity. Fig. 2 shows SEM surface morphology of the original GDL [28] while Fig. 3 depicts the GDL morphologies after the sodium chloride experimental tests. Fig. 3 shows the GDL morphologies with three NaCl mass concentrations (i.e., 300 mg/L, 400 mg/L and 500 mg/L) and six testing periods (i.e., 24h, 72h, 144h, 216h, 288h, 360h).

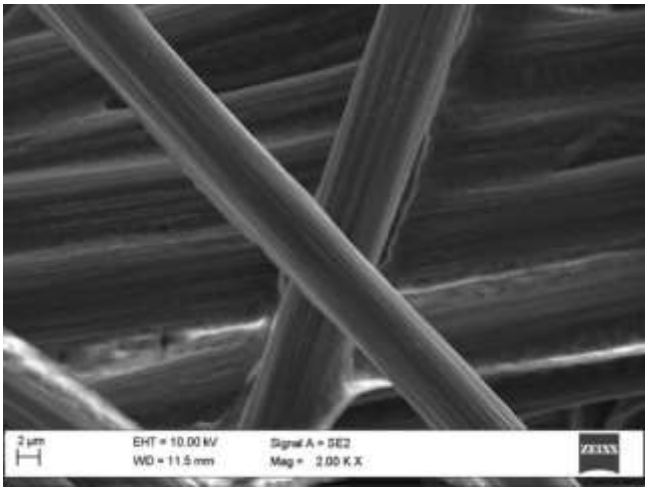


Fig. 2. SEM surface morphology of original GDL.

Comparing Fig. 2 and Fig. 3 one can note that the sodium chloride crystal particles appears in all the tested GDL morphologies. As the testing time increases, the number of the NaCl crystal particles significantly increases and the particle distribution changes from sparse to dense quantity. The most striking feature is that the sodium chloride crystals are uniformly distributed at the carbon fibers and bonds and the crystal dense increases with time; with different NaCl mass concentrations, the sodium chloride crystal particles are randomly distributed on the carbon fibers.

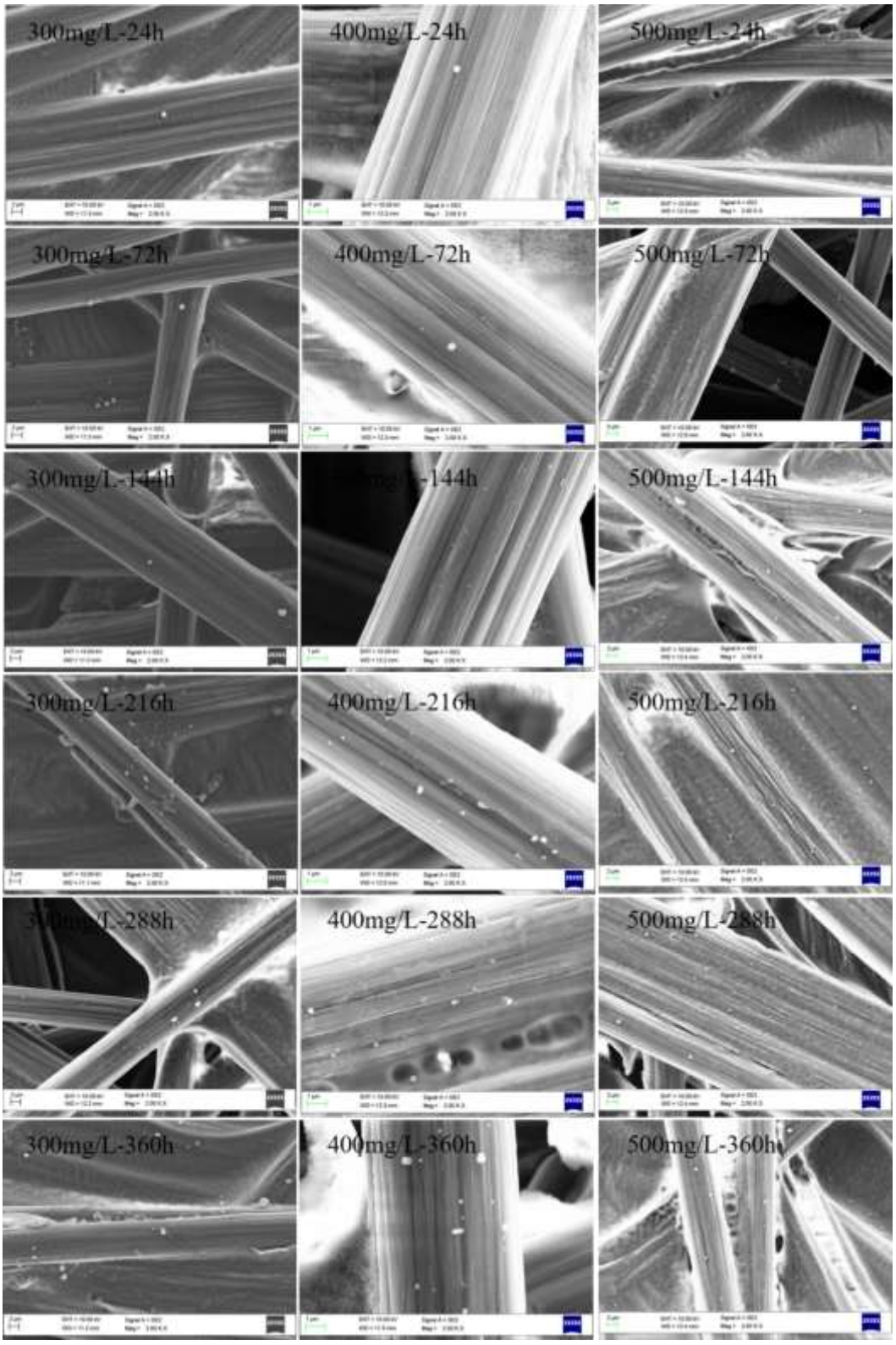
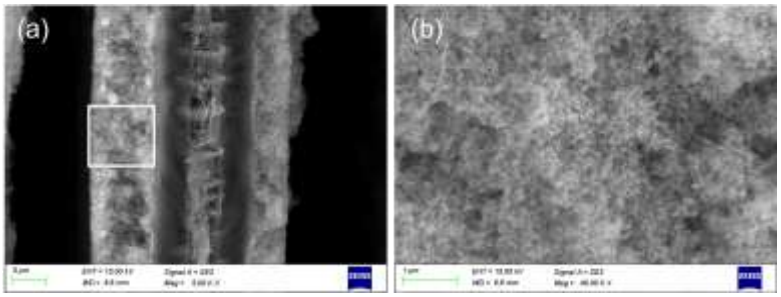


Fig. 3. Surface morphologies of the GDL with different experimental conditions.

The surface morphologies of the GDLs of the membrane electrodes observed by the electron microscopy demonstrate that the sodium chloride crystal particles are uniformly distributed in the salt spray environment. The overall shape of the crystal particles is regular and shows a typical cubic crystal structure. The distribution of the crystal particles becomes more and more extensive and dense

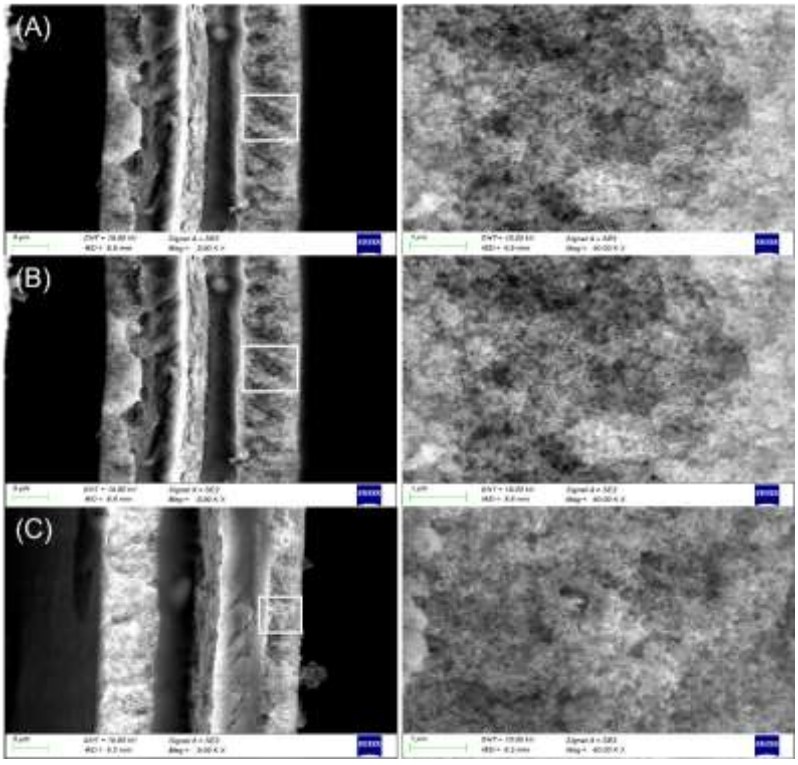
with increasing experimental time at a certain NaCl mass concentration, while the number of crystals varies more significantly with different NaCl mass concentrations at a certain testing time.

In order to further investigate the concentration dispersion characteristics of the sodium chloride at the PEMFC membrane electrodes in the salt spray condition, one testing sample contaminated with the sodium chloride is tested for 360h. The base sample is a cross-sectional microstructure of the uncontaminated membrane electrode. The cross-sectional microstructures of the CCM layer and the membrane electrode and the CCM structure are observed under 15 kV voltage. Fig. 4 manifests the cross-sectional microstructure of the original CCM and Fig. 5 depicts the cross-sectional microstructure of the tested CCM.



(a) Magnification 5KX (b) Magnification 40KX

Fig. 4. Cross-sectional morphology of original CCM.



(A) 360h-300mg/L; (B) 360h-400mg/L; (C)360h-500mg/L

Fig. 5. Cross-sectional morphology of tested CCM with five different Cal mass concentrations.

As can be seen in Fig. 5, different from the surface morphologies of the GDL in Fig. 3, the sodium chloride crystals are not observed. The cross-sectional morphologies do not present any crystal attachments at the magnification of both 5 KX and 40 KX; and no crystal structure is found after 360h of testing at the concentrations of 300 mg/L, 400 mg/L and 500 mg/L in the salt spray environment. It is inferred that the sodium chloride may appear in the catalytic layer and the membrane in ionic form. Comparing the CCM surface morphologies before and after the tests in Fig. 4 and Fig. 5, it can observe that the 360h testing does not cause any visibly morphological changes on the microscopic morphology.

Fig. 6 shows the elements and their distributions in the cross sections of the tested membrane electrodes. In Fig. 6(a) because the membrane electrode is without any treatment, no sodium or chloride elements are found in the elemental distribution. However, the elemental distribution of the membrane electrodes tested by the 500 mg/L NaCl mass concentration in a salt spray environment is significantly different from Fig. 6(a). The elemental distributions of the sodium and chloride elements in Fig. 6(b)-(d) suggest the presence of the sodium in the membrane and the chlorine in the catalytic layer. One can note that the sodium and chloride elements are distributed in a homogeneous distribution across the proton exchange membrane and catalytic layer; and they are not distributed in the same position but in a dispersed manner.

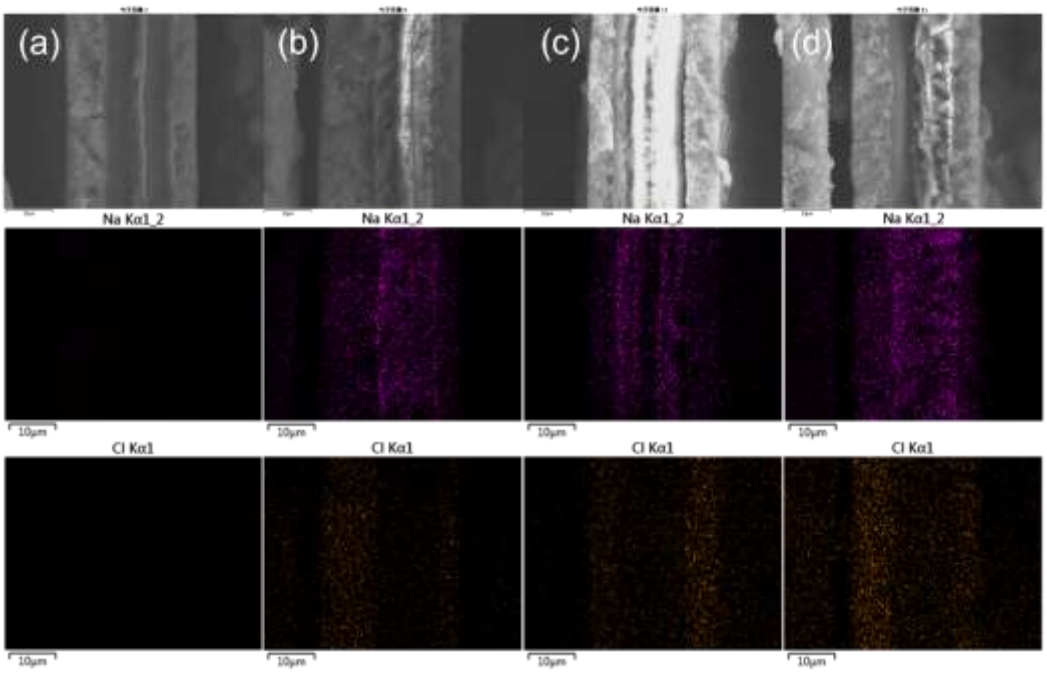


Fig. 6. Elemental distributions of the membrane electrodes: (a) Original membrane electrode; (b) membrane electrode tested by 24h; (c)144h; (d) 288h

Fig. 6 also suggests that the sodium chloride crystal structure is attached to the GDL, but the crystal structure is not found on the catalytic layer and the proton exchange membrane. Therefore, it is clear that the sodium chloride elements appear in two forms: one is the sodium chloride crystal form on the gas diffusion layer and the other is the ions form on the catalytic and proton exchange membranes.

Fig. 7 depicts the cross-sectional morphology of the CCM after 360h testing in a salt spray environment with a NaCl mass concentration of 500 mg/L and Fig. 8 shows the elements distribution curves of the cross section. It can observe that in Fig. 8(a) the element F fluctuates at a distance of 5 to 20 um and forms three peaks; the element Pt forms two peaks and the peak values are about 100cps at 2.6μm and 300cps at 27.5μm, respectively; the element Cl appears three peaks appear between 5μm and 22.5μm with a maximum peak value of about 80cps; and the overall distribution curve of the element Na is similar to that of the element Cl but with much smaller peaks.

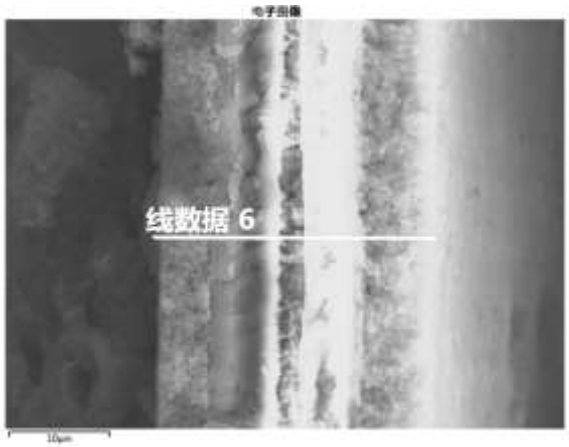


Fig. 7. Location of the cross section of the CMM after 360h testing.

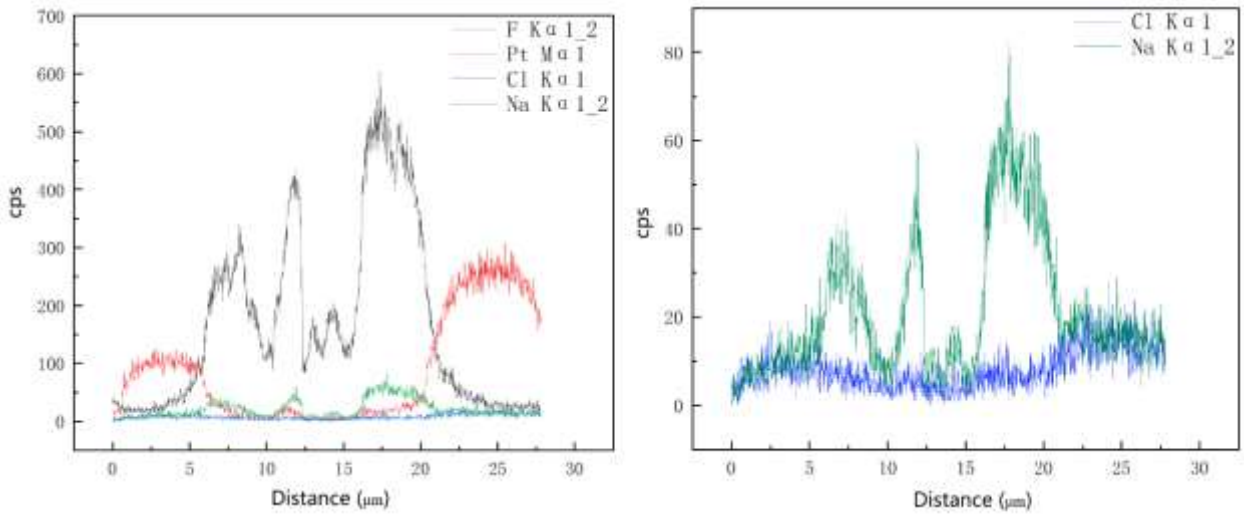
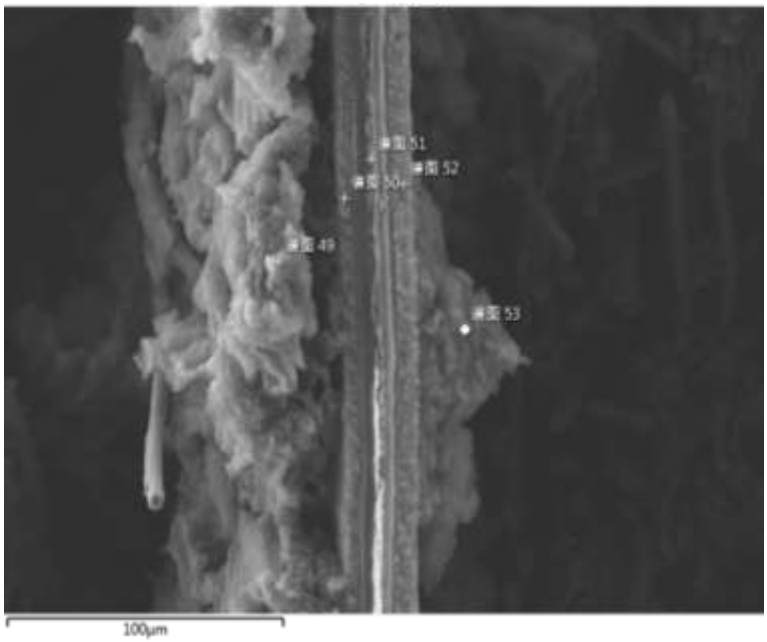


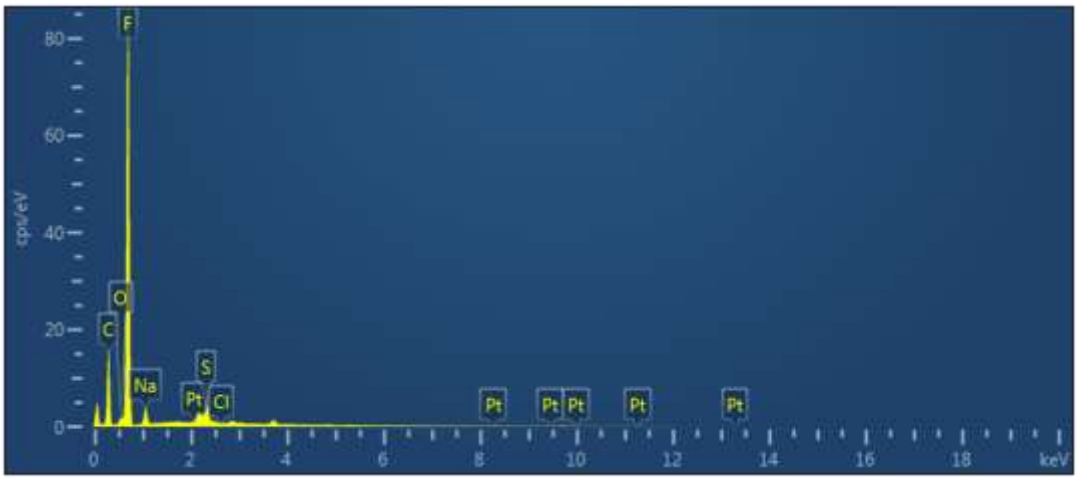
Fig. 8. Elements distribution curves of the cross section.

3. Evaluation of Sodium Chlorine Contamination

3.1. Elements Contents

In the element analysis of the membrane microstructure, in order to detect the relative content of each element, the element spot analysis method is performed. A sample in 300h-500mg/L condition is used to interpret the element spot position and element content spectrum, as shown in Fig. 9 and Table 2. It can be seen that the elements of C, O, Na, Pt, S and Cl are detected. The C and O contents account for the largest percentages in the GDL, PEM and catalytic layer; followed by the F content; the content of Na is larger than that of Cl and S.





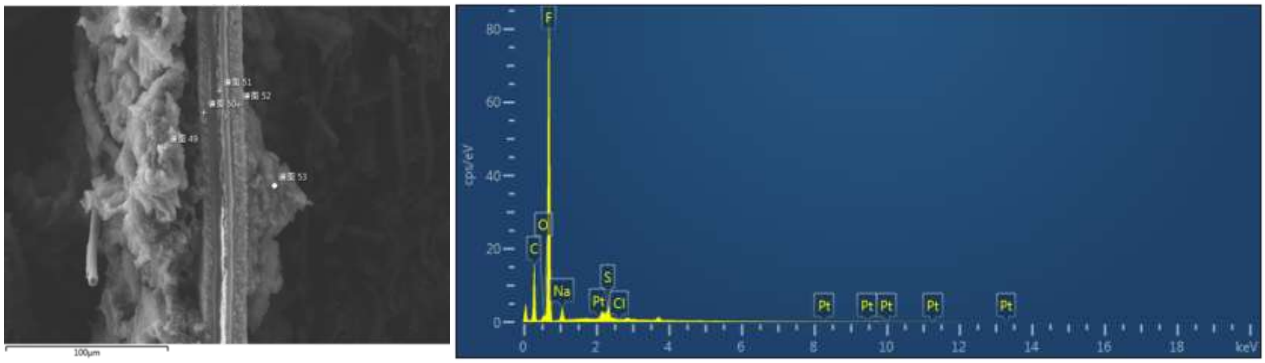


Fig. 9. Energy spectrum of spot analysis in the membrane.

Table 2. Element contents results

	C	F	Pt	Na	Cl	O	S
GDL anode	95.47%	1.20%	0	0.01%	0.01%	3.32%	0%
GDL cathode	93.26%	2.39%	0	0.04%	0.03%	4.29%%	0
PEM	31.53%	61.5%	0	2.92%	0	2.83%	1.21%
Anode of catalytic layer	76.51%	17.22%	1.86%	0.57%	0.08%	3.34%	0.41%
Cathode of catalytic layer	70.16%	17.2%	3.57%	0.52%	0.14%	8.40%	0.01%

Table 3 manifests the elements contents in the membrane with respect to varying time and Table 4 displays the concentration effect. It can be seen that the percentage content of the sodium in the membrane becomes larger with increasing test time and concentration; at 24h-500mg/L testing the sodium percentage content is 0.64% in the membrane and this value increases to 2.92% at 360h-500mg/L testing in Table 3; at 100mg/L-360h testing the sodium percentage content is 1.61% in the membrane and this value increases to 2.92% at 500mg/L-360h testing in Table 4. However, the chlorine content does not show any change rule in the membrane with respect to testing time and solution concentration.

Table 3. Elements percentage contents in time-varying condition

500mg/L	24h	72h	144h	216h	288h	360h
C	32.93%	42.52%	48.67%	46.26%	34.95%	31.53%
F	62.6%	52.9%	44%	48.5%	58%	61.5%
Pt	0.22%	0.05%	0.12%	0	0	0
Na	0.64%	1.3%	1.58%	1.94%	2.45%	2.92%
Cl	0.01%	0	0.05%	0	0	0
O	2.45%	2.16%	5.09%	2.54%	2.44%	2.83%
S	1.16%	1.08%	0.59%	0.75%	1.75%	1.21%

Table 4. Elements percentage contents in different solution concentrations

360h	100mg/L	200mg/L	300mg/L	400mg/L	500mg/L

C	38.04%	20.91%	30.11%	31.71%	31.53%
F	56.06%	68.6%	63.07%	62.56%	61.5%
Pt	0.01%	0.08%	0.02%	0.04%	0
Na	1.61%	2.38%	2.56%	2.86%	2.92%
Cl	0.01%	0.03%	0.01%	0.01%	0
O	1.75%	3.38%	2.92%	1.95%	2.83%
S	2.53%	4.62%	1.11%	0.86%	1.21%

3.2 Evaluation of Membrane Contamination Degree

The affinity of the membranes is critical to different concentrations of contaminants; and hence, it is important to evaluate the contaminant degree in the membranes. For this purpose, this study adopts two steps to qualify and quantify the contaminant degree. In the first step, qualitative analysis is carried out to qualify the contaminant degree based on the experimental results of the microscopic characterization. In Table 3 and Table 4 one can note that the sodium content in the proton exchange membranes increases with increasing time and solution concentration and the chloride ions are hardly absorbed into the membrane. As a result, the degree of membrane contamination can be evaluated by the sodium content. For this reason, the sodium to fluorine ratio is proposed as an evaluation merit to qualify the membrane contamination. The sodium to fluorine ratio in the membranes measured by the EDX is summarized in Table 5. The EDX results show that as the NaCl mass concentration increases, the absorption of sodium ions in the membranes increases and the sodium to fluorine ratio gradually increases; similarly, the sodium to fluorine ratio in the membranes gradually increases with the increase of the testing time. These observations suggest that the increase of both the testing time and NaCl mass concentration will lead to the increase of the impurity absorption by the membrane and the increase of the sodium to fluorine ratio. As a result, the larger the sodium to fluorine ratio, the heavier the contaminant degree in the membrane.

Table 5. Sodium to fluorine ratio

Testing time	Na/F ratio	NaCl mass concentration	Na/F ratio
24h	1.02×10^{-2}	100mg/L	2.87×10^{-2}
72h	2.46×10^{-2}	200mg/L	3.47×10^{-2}
144h	3.59×10^{-2}	300mg/L	4.06×10^{-2}
216h	4.00×10^{-2}	400mg/L	4.57×10^{-2}
288h	4.22×10^{-2}	500mg/L	4.75×10^{-2}
360h	4.75×10^{-2}	—	—

In the second step, quantitative analysis is carried out to quantify the contaminant degree by

developing a diffusion rate prediction model for sodium contamination in the membrane. The prediction model that considers the testing time and NaCl mass concentration factors is expressed in Eq. (1) [29].

$$W = W_j(C, t) \tag{1}$$

where, W is the membrane contaminant degree, W_j is a prediction function related to the NaCl mass concentration C and the testing time t in the salt spray environment.

The prediction function can be established by regressing the sodium mass percentage in the experimental tests [31-33].

$$W_j(C, t) = \mathrm{K}_c \cdot K_t \tag{2}$$

where K_c denotes the change rate of the sodium mass percentage with respect to the NaCl mass concentration and K_t denotes the change rate of the sodium mass percentage with respect to time.

K_c can be estimated by fitting the experimental data using the least squares method. Fig. 10 shows the fitting results that describing the relationship between the sodium mass percentage and the solution contamination concentrations.

Similarly, K_t can be estimated according to Table 6 using the least squares method. The fitting result is shown in Fig. 11.

$$k_t = 0.0024 + 3.9244 \times 10^{-6} t \tag{3}$$

Combining Eq. (2) and Eq. (3), it yields

$$W_j(C, t) = \left(0.0024 + 3.9244 \times 10^{-6} t\right) \cdot k_c \tag{4}$$

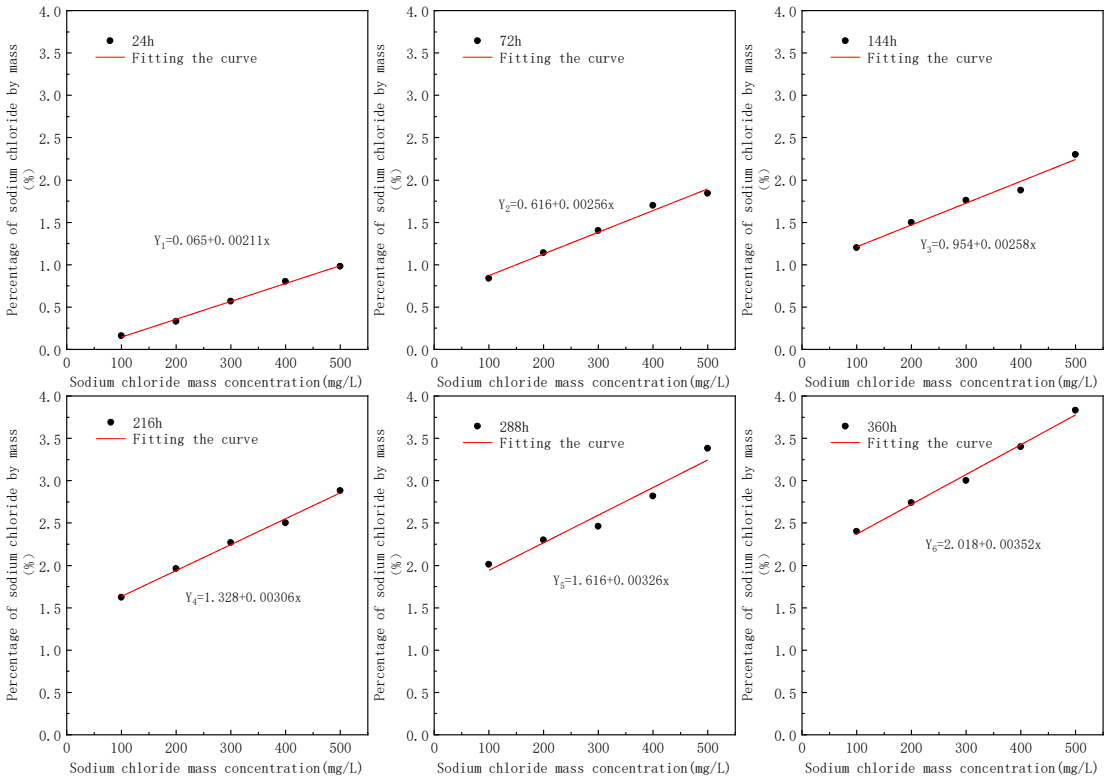


Fig. 10. Fitting curve of sodium mass percentage to concentration

Table 6. Sodium mass percentage in the membrane

	24h	72h	144h	216h	288h	360h
100mg/L	0.16%	0.84%	1.2%	1.62%	2.01%	2.4%
200mg/L	0.33%	1.14%	1.5%	1.96%	2.3%	2.74%
300mg/L	0.57%	1.4%	1.76%	2.27%	2.46%	3.0%
400mg/L	0.8%	1.7%	1.88%	2.5%	2.82%	3.4%
500mg/L	0.98%	1.84%	2.3%	2.88%	3.38%	3.83%

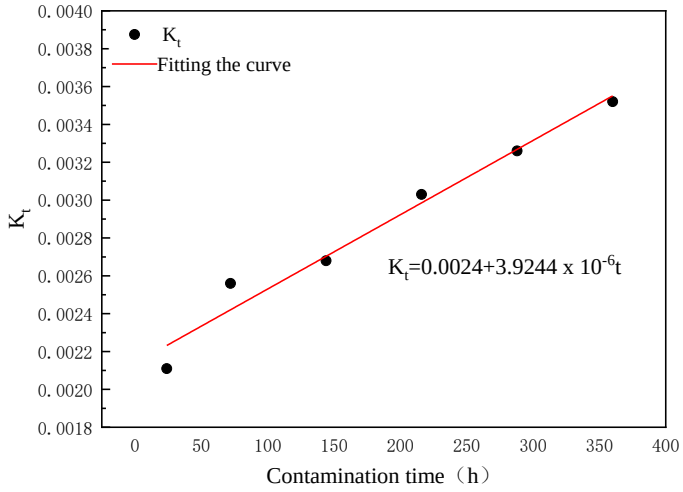


Fig. 11. Fitting curve of the sodium mass percentage to time.

Eq. (4) can be used as an empirical model to predict the sodium mass percentage in the proton exchange membrane. Assuming that the total mass in the test area of the PEMFC membrane electrode remains constant, the relationship between the sodium mass percentage to total element mass can be expressed as

$$W_j = \frac{m_{Na}}{m_{Na}+m} \tag{5}$$

where m_{Na} is the sodium mass and m is the total element mass in the test area.

Combining (4) and (5) it obtains

$$m_{Na} = \frac{(0.0024+3.9244\times10^{-6}t)\cdot k_c}{1-(0.0024+3.9244\times10^{-6}t)\cdot k_c}\cdot m \tag{6}$$

If the concentration is determined, the sodium diffusion rate can be obtained according to the principle of partial derivatives.

$$V_{N_a} = \frac{d[m_{Na}]}{dt} \tag{7}$$

Combining (6) and (7) the sodium diffusion rate can be rewritten as

$$V_{N_a} = \frac{\partial m_{Na}}{\partial t} = \frac{3.9244\times10^{-6}k_c m}{[1-(0.0024+3.9244\times10^{-6}t)k_c]^2} \tag{8}$$

As a result, the diffusion rate prediction model for sodium in the membrane is obtained to quantify the membrane contamination degree.

4. Conclusions

This work experimentally explores the influence of the sodium chloride pollution on the PEMFC performance in the marine salt spray environment by analyzing the concentration diffusion characteristics of the sodium chloride in the PEMFC membrane electrodes. The findings of the experimental results demonstrate that:

(1) Sodium chloride appears on the membrane electrode in two ways, as crystals on the gas diffusion layer structure and as ions on the catalytic layer and the proton exchange membrane structure. The crystals are uniformly distributed on the carbon fibers of the gas diffusion layer in the salt spray environment, and the crystal distribution becomes more and more dense with time, but the crystal particle size does not grow significantly.

(2) The effect of sodium chloride on each structure of the membrane electrode is different, and the percentage content of sodium atoms detected on the proton exchange membrane structure is up to 2.92 %. The atomic percentage content is positively correlated with the experimental time and concentration. the sodium element distribution curve presents a similar distribution trend to that of the F element. The overall sodium content is detected to be higher than that of chlorine element.

(3) Based on the experimental test result data, a quantitative relationship is established to evaluate the contamination degree of the membrane electrode. The linear fitting method in the least squares method is used to propose the relationship between the diffusion rate of sodium elements in the membrane, the contamination time and the contamination concentration under the salt spray environment, and to construct a prediction model for the diffusion rate of contaminated ions that can be used in the actual working conditions under the action of cell operation time and salt spray salt content.

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this article.

Research Data

All the data can be requested from the corresponding author.

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